

PATENT COOPERATION TREATY

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference TS 6648 PCT	FOR FURTHER ACTION see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.	
International application No. PCT/EP 00/ 06354	International filing date (day/month/year) 04/07/2000	(Earliest) Priority Date (day/month/year) 05/07/1999
Applicant SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 3 sheets.
☒ It is also accompanied by a copy of each prior art document cited in this report.

1. Basis of the report

- a. With regard to the **language**, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

☐ the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

- b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing :

☐ contained in the international application in written form.

☐ filed together with the international application in computer readable form.

☐ furnished subsequently to this Authority in written form.

☐ furnished subsequently to this Authority in computer readable form.

☐ the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

☐ the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2. ☐ **Certain claims were found unsearchable** (See Box I).

3. ☐ **Unity of invention is lacking** (see Box II).

4. With regard to the **title**,

☒ the text is approved as submitted by the applicant.

☐ the text has been established by this Authority to read as follows:

5. With regard to the **abstract**,

☒ the text is approved as submitted by the applicant.

☐ the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the **drawings** to be published with the abstract is Figure No.

☐ as suggested by the applicant.

☐ because the applicant failed to suggest a figure.

☐ because this figure better characterizes the invention.

NONE _____

☒ None of the figures.

INTERNATIONAL SEARCH REPORT

International Application No

PCT 00/06354

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 B65D39/00 C08J9/00 C08L53/00 C08L23/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B65D C08J C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, CHEM ABS Data, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	WO 00 26103 A (PLIMMER PETER N ; SUPREME CORQ INC (US); ZECH JEROME M JR (US)) 11 May 2000 (2000-05-11) claims; examples ---	1-10
P,X	WO 00 12592 A (SHELL INT RESEARCH) 9 March 2000 (2000-03-09) claims; examples ---	1-10
X	US 5 496 862 A (BURNS DENNIS L) 5 March 1996 (1996-03-05) cited in the application column 3, line 60 - line 67; figures column 4, line 53 - line 63 column 5, line 53 - column 6, line 2; claims --- -/--	1-6,8-10

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

* & * document member of the same patent family

Date of the actual completion of the international search

24 November 2000

Date of mailing of the international search report

05/12/2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
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Fax: (+31-70) 340-3016

Authorized officer

DE LOS ARCOS, E

INTERNATIONAL SEARCH REPORT

International Application No

PCT 00/06354

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 1 196 125 A (W.R. GRACE & CO.) 24 June 1970 (1970-06-24) page 1, line 46 - line 72 page 1, line 86 - page 2, line 6 page 2, line 83 - line 86; claims; examples 2,3,5,6 ---	1-5,7-10
X	US 4 764 535 A (LEICHT LARRY F) 16 August 1988 (1988-08-16) cited in the application claims; tables I-IV ---	1-10
X	DATABASE WPI Section Ch, Week 199510 Derwent Publications Ltd., London, GB; Class A13, AN 1995-070424 XP002153392 & JP 06 345914 A (ASAHI KASEI KOGYO KK), 20 December 1994 (1994-12-20) abstract ---	1,9,10
A	US 3 686 364 A (ROBINSON KEITH J ET AL) 22 August 1972 (1972-08-22) claims; examples -----	1,9,10

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT 00/06354

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 0026103 A	11-05-2000	AU 1340400 A	22-05-2000
WO 0012592 A	09-03-2000	AU 5973699 A US 6127444 A	21-03-2000 03-10-2000
US 5496862 A	05-03-1996	AU 2387099 A AU 691497 B AU 6783894 A BG 100118 A BR 9406394 A CA 2161673 A CN 1124968 A CZ 9502880 A EP 0698054 A FI 955287 A HU 73270 A JP 9500074 T NO 954417 A NZ 266368 A PL 311642 A RO 115528 B RU 2127699 C SK 136995 A WO 9425513 A US 5480915 A US 6127437 A US 5692629 A US 5710184 A US 5855287 A	10-06-1999 21-05-1998 21-11-1994 31-07-1996 13-02-1996 10-11-1994 19-06-1996 14-02-1996 28-02-1996 03-01-1996 29-07-1996 07-01-1997 03-01-1996 26-11-1996 04-03-1996 30-03-2000 20-03-1999 04-12-1996 10-11-1994 02-01-1996 03-10-2000 02-12-1997 20-01-1998 05-01-1999
GB 1196125 A	24-06-1970	BE 704544 A DE 1720114 A DK 124073 B FR 1539380 A FR 1557686 A NL 6713322 A, B	01-02-1968 23-12-1970 11-09-1972 21-02-1969 01-04-1968
US 4764535 A	16-08-1988	CA 1285697 A US 4677133 A	02-07-1991 30-06-1987
JP 6345914 A	20-12-1994	NONE	
US 3686364 A	22-08-1972	BE 744975 A CA 857965 A CH 519534 A DE 2002579 A FR 2029555 A GB 1250088 A NL 7000723 A, B,	27-07-1970 08-12-1970 29-02-1972 03-09-1970 23-10-1970 20-10-1971 30-07-1970

PATENT COOPERATION TREATY

PCT

NOTIFICATION OF ELECTION

(PCT Rule 61.2)

From the INTERNATIONAL BUREAU

To:

Commissioner
 US Department of Commerce
 United States Patent and Trademark
 Office, PCT
 2011 South Clark Place Room
 CP2/5C24
 Arlington, VA 22202
 ETATS-UNIS D'AMERIQUE
 in its capacity as elected Office

Date of mailing (day/month/year) 14 March 2001 (14.03.01)	
International application No. PCT/EP00/06354	Applicant's or agent's file reference TS 6648 PCT
International filing date (day/month/year) 04 July 2000 (04.07.00)	Priority date (day/month/year) 05 July 1999 (05.07.99)
Applicant COIGNOUL, Emanuelle et al	

1. The designated Office is hereby notified of its election made:

☒ in the demand filed with the International Preliminary Examining Authority on:
 30 January 2001 (30.01.01)

☐ in a notice effecting later election filed with the International Bureau on:

2. The election ☒ was
☐ was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland Facsimile No.: (41-22) 740.14.35	Authorized officer Pascal Piriou Telephone No.: (41-22) 338.83.38
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PATENT COOPERATION TREATY

PCT

From the INTERNATIONAL BUREAU

NOTIFICATION OF THE RECORDING
OF A CHANGE(PCT Rule 92bis.1 and
Administrative Instructions, Section 422)

To:

KORTEKAAS, M., C., J., A.
Kraton Polymers Research B.V.
Badhuisweg 3
NL-1031 CM Amsterdam
PAYS-BAS

Date of mailing (day/month/year) 07 January 2002 (07.01.02)	
Applicant's or agent's file reference TS 6648 PCT	IMPORTANT NOTIFICATION
International application No. PCT/EP00/06354	International filing date (day/month/year) 04 July 2000 (04.07.00)

1. The following indications appeared on record concerning:			
<input checked="" type="checkbox"/> the applicant	<input type="checkbox"/> the inventor	<input type="checkbox"/> the agent	<input type="checkbox"/> the common representative
Name and Address SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V. Carel van Bylandtlaan 30 NL-2596 HR The Hague Netherlands		State of Nationality NL	State of Residence NL
		Telephone No. 31 20 630 2197	
		Facsimile No. 31 20 630 2034	
		Teleprinter No.	
2. The International Bureau hereby notifies the applicant that the following change has been recorded concerning:			
<input checked="" type="checkbox"/> the person	<input type="checkbox"/> the name	<input type="checkbox"/> the address	<input type="checkbox"/> the nationality <input type="checkbox"/> the residence
Name and Address KRATON POLYMERS RESEARCH B.V. Badhuisweg 3 NL-1031 CM Amsterdam Netherlands		State of Nationality NL	State of Residence NL
		Telephone No. 31 20 630 2197	
		Facsimile No. 31 20 630 2034	
		Teleprinter No.	
3. Further observations, if necessary: Please note that the address for correspondence has also been changed accordingly.			
4. A copy of this notification has been sent to:			
<input checked="" type="checkbox"/> the receiving Office	<input type="checkbox"/> the designated Offices concerned		
<input type="checkbox"/> the International Searching Authority	<input checked="" type="checkbox"/> the elected Offices concerned		
<input checked="" type="checkbox"/> the International Preliminary Examining Authority	<input type="checkbox"/> other:		

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland Facsimile No.: (41-22) 740.14.35	Authorized officer S. Buttay Telephone No.: (41-22) 338.83.38
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PATENT COOPERATION TREATY

PCT

NOTIFICATION OF THE RECORDING
OF A CHANGE(PCT Rule 92bis.1 and
Administrative Instructions, Section 422)

From the INTERNATIONAL BUREAU

To:

KORTEKAAS, M., C., J., A.
Kraton Polymers Research B.V.
Intellectual Property Services
P.O. Box 37666
NL-1030 BH Amsterdam
PAYS-BAS

Date of mailing (day/month/year) 05 février 2002 (05.02.02)	IMPORTANT NOTIFICATION
Applicant's or agent's file reference TS 6648 PCT	
International application No. PCT/EP00/06354	International filing date (day/month/year) 04 juillet 2000 (04.07.00)

1. The following indications appeared on record concerning:

☒ the applicant ☐ the inventor ☐ the agent ☐ the common representative

Name and Address

SHELL INTERNATIONALE RESEARCH
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2. The International Bureau hereby notifies the applicant that the following change has been recorded concerning:

☐ the person ☐ the name ☐ the address ☐ the nationality ☐ the residence

Name and Address

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Facsimile No.

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Teleprinter No.

3. Further observations, if necessary:

Corrected version of form PCT/IB/306 fo 07 January 2002: Please note the address for correspondence.

4. A copy of this notification has been sent to:

<input checked="" type="checkbox"/> the receiving Office	<input type="checkbox"/> the designated Offices concerned
<input type="checkbox"/> the International Searching Authority	<input checked="" type="checkbox"/> the elected Offices concerned
<input checked="" type="checkbox"/> the International Preliminary Examining Authority	<input type="checkbox"/> other:

The International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland

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Authorized officer

Dorothee MÜLHAUSEN

Telephone No.: (41-22) 338.83.38

10/030438

m-j

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

CORRECTED VERSION

(19) World Intellectual Property Organization
International Bureau(43) International Publication Date
11 January 2001 (11.01.2001)

PCT

(10) International Publication Number
WO 01/002263 A1(51) International Patent Classification⁷: **B65D 39/00**,
C08J 9/00, C08L 53/00, 23/02

(21) International Application Number: PCT/EP00/06354

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(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
99305309.9 5 July 1999 (05.07.1999) EP(71) Applicant (for all designated States except US): **KRATON
POLYMERS RESEARCH B.V.** [NL/NL]; Badhuisweg 3,
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(72) Inventors; and

(75) Inventors/Applicants (for US only): **COIGNOUL**,
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[FR/BE]; Avenue Jean Monnet 1, B-1348 Ottignies,
Louvain-La-Neuve (BE).(81) Designated States (national): AE, AG, AL, AM, AT, AU,
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ,DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR,
HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR,
LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ,
NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM,
TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.(84) Designated States (regional): ARIPO patent (GH, GM,
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian
patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European
patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE,
IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG,
CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report

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6 September 2002

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see PCT Gazette No. 36/2002 of 6 September 2002, Sec-
tion IIFor two-letter codes and other abbreviations, refer to the "Guid-
ance Notes on Codes and Abbreviations" appearing at the begin-
ning of each regular issue of the PCT Gazette.

(54) Title: SYNTHETIC BOTTLE STOPPER

(57) Abstract: The present invention provides a synthetic bottle stopper made from a foamed thermoplastic elastomer composition comprising: a) one or more thermoplastic block copolymers c) a blowing agent, and optionally d) one or more plasticisers, characterised in that the composition further comprises b) one or more branched polyolefins having a melt flow index of from 0.05 to 400 (at 2.16 kg/190 °C, determined in accordance with ASTM D 1238).

WO 01/002263 A1

SYNTHETIC BOTTLE STOPPER

Field of the Invention

The present invention relates to a synthetic bottle stopper. More in particular, the present invention relates to a bottle stopper made from a foamed thermoplastic elastomer comprising one or more thermoplastic block copolymers and a blowing agent.

Background of the invention

Cork is a natural occurring material regularly used for the production of stoppers for casks, vials and bottles (also referred to as "bung" or "moulded closure for a liquid container", etc.). Cork has a good grip on glass, and requires an appropriate force of about 250-430 N to pull off the cork from a bottle. Stoppers made of cork can be used for closing a half-used bottle for a second time. Besides, swell of cork stoppers when in contact with wine improves their grip. Also, cork is a light material (density of about 0.22 kg/m^3), which is important to control the cost when transporting the cork and/or the bottles wherein the cork stoppers are used. Cork is hence a popular material in the production of stoppers.

However, stoppers made of cork may become infected by fungi and bacteria, and they may impart undesired flavour and colour to the contents of the vials and bottles wherein they are used. Moreover, good quality cork is becoming rare and hence expensive. Accordingly, synthetic bottle stoppers have been developed.

Obviously, these synthetic bottle stoppers need to perform similar to cork as regards the elasticity of the material, long term creep, good control during insertion and manufacture, and possibility of reinsertion. Most

importantly, they need to be light, i.e., have a density of less than about 0.7 kg/m³, preferably of about 0.5 kg/m³.

Synthetic stoppers for vials and bottles are known.

5 International application 99/01354 (Supreme Corq) discloses a synthetic cork for removable insertion into an opening of a bottle comprising a hard plastic top and a shaft made of a thermoplastic elastomer (TPE) combined with a blowing agent, wherein the TPE consists of one or
10 more styrenic block copolymers. Suitable styrenic block copolymers are selected from the group corresponding to the general formulae A-B or A-B-A, wherein "A" represents a polystyrene block and "B" represents a polybutadiene block, a polyisoprene block, a hydrogenated polybutadiene
15 block or a hydrogenated polyisoprene block. Suitable blowing agents comprise azodicarbonamide or a masterbatch thereof sold under the tradename "SPECTRATECH FM1150H", ozodecarbonoxide and sodium bicarbonate. The mixture used for forming the shaft may also incorporate a minor amount
20 of low density polypropylene.

International application 94/25513 is an earlier application by Supreme Corq, disclosing a synthetic cork (referred to as "molded closure for a liquid container") comprising the TPE and blowing agent mentioned above.

25 US patent No. 3,984,022 (assigned to Le Bouchage Mécanique) discloses a bottle stopper of biconical configuration, which is made from a foamed plastic with a dense outer layer enclosing a closed cellular or honeycomb structure around the centre. The stopper is
30 produced by injection of a plastic material, which may be a polyolefin such as polyethylene or EVA (ethylene-vinyl acetate), with a pore-forming additive into a mould.

US patent No. 4,499,141 (assigned to the Coca Cola Company) discloses a plastic closure for sealing liquid
35 product containers wherein a synthetic cork article is

prepared from a thermoplastic resin and a blowing agent, e.g., azodicarbonamide, and whereby the plastic article is injection moulded.

US patent No. 4,188,457 (assigned to Metal Box Limited.) discloses a "bung" for closing a wine bottle in the manner of a cork, which is formed in a conventional injection-moulding machine from ethylene-vinyl acetate copolymer (EVA) with the addition of sodium meta-bisulphite and sodium bicarbonate.

These synthetic bottle stoppers, however, are either too dense and/or too hard. As a result, these bottle stoppers will be difficult to insert (problem of leakage), and to remove (in one piece) with an ordinary corkscrew. Moreover, it may be difficult to insert a corkscrew if the stopper is too hard. Besides, these synthetic stoppers (or at least those of Supreme Corq) require the presence of a plasticiser in the form of an oil. If no or too little oil is used, then the thermoplastic elastomer composition will be too viscous and the cells therein will not be able to expand. The end-result is a dense "foam". If too much oil is used, then the viscosity will be too low and cells collapse, with the same end-result. Such bottle stoppers therefore require a precise operating window (about 30-40 parts per hundred parts of elastomer). Unfortunately, oil is a potential contaminant of the contents of the bottle. There is therefore a demand for a new foamed thermoplastic elastomer composition that provides synthetic bottle stoppers of suitable density, and that requires no or only a little oil as plasticiser.

Summary of the invention

The present invention provides a synthetic bottle stopper made from a foamed thermoplastic elastomer composition comprising

- a) one or more thermoplastic block copolymers
 - c) a blowing agent, and optionally
 - d) one or more plasticisers,
- characterised in that the composition further comprises
- b) one or more branched polyolefins having a melt flow index ('MFI') of from 0.05 to 400 (at 2.16 kg/190 °C, determined in accordance with ASTM D 1238).

Detailed description of the invention

The synthesis of foamed TPE compositions is known. In addition to the references cited herein before, such compositions are described in Japanese patent application No. 58173146 (Yokohama Rubber KK, Derwent abstract No. 83-822911/47). This reference describes a composition comprising a thermoplastic block copolymer and a thermoplastic resin and/or plasticizer or softener. The composition forms a non-adhesive foaming material and can be used as a packing or gasket material.

In US patent No. 4,764,535 (assigned to Q'SO Inc.) a composition is described comprising a mixture of two thermoplastic elastomers, a nucleating agent and an unstable resin. The compositions may be employed in formulating coatings, laminates, hot melt adhesives and caulking compounds.

Hot melt compositions from which foamed products can be obtained are disclosed in US patent No. 4,529,740 (assigned to W.R. Grace & Co.). The compositions include a thermoplastic elastomer, a small amount of a salt of a sulfonated styrene polymer, and a blowing agent. The composition may be used to produce foamed products suited for example as sealants in closures for containers.

Plastic foam products are also disclosed in US patent No. 5,585,411 and International application No. 94/28066 (both to Shell). In the former, a plastic foam is disclosed that is made from a blend comprising poly-1-butene, a styrenic block or star copolymer, and/or an

olefinic rubber, and optionally a non-elastomeric polyolefin. These foams are particularly useful in very high temperature applications such as pipe wrap in refrigerators. In the latter a novel elastomeric poly-1-butene is described, as well as blends thereof with compatible materials, which are particularly suitable in textile and fibre applications, and blends thereof with incompatible materials, which are particularly useful in easy-open packaging applications, in foam applications and in PVC replacement.

The use of a composition as described in claim 1 for the purpose of preparing a superior synthetic bottle stopper is neither disclosed nor hinted at in any of these references. The components of the composition are described in more detail herein after.

Component a)

The expression "thermoplastic block copolymer" refers to a polymer having two or more distinguishable polymer blocks, of which at least one is glassy or crystalline at service temperature but fluid at higher temperatures, and at least one of which is elastomeric (rubbery) at service temperature. A comprehensive review on such polymers is provided by Messrs. Legge, Holden and Schroeder, in "Thermoplastic Elastomers", published by Hanser Publishers in 1987 (ISBN 3-446-14827-2). Such polymers include thermoplastic polyurethane elastomers and various other block copolymers.

The preferred thermoplastic block copolymers in accordance with the present invention, are styrenic block copolymers, i.e., wherein the or each glassy polymer block of the block copolymer is made of polymerized vinylaromatic monomer, such as styrene, in an amount of at least 80 mole % on the total monomer content of the glassy polymer block. Styrene is the preferred vinylaromatic monomer, but other suitable vinylaromatic

monomers include α -methylstyrene, p-methylstyrene, m-methylstyrene, o-methylstyrene, p-tert-butylstyrene, dimethylstyrene, and various other alkyl-substituted styrenes, alkoxy-substituted styrenes, vinyl naphthalene and vinyl xylene. The alkyl and alkoxy groups of the alkyl-substituted or alkoxy substituted styrenes respectively preferably contain from 1 to 6 carbon atoms, more preferably from 1 to 4 carbon atoms. Comonomers, if present, may be selected from (di)olefins and other compounds copolymerizable with styrene.

Preferred styrenic block copolymers are those wherein the or each elastomeric polymer block of the block copolymer is made of polymerized conjugated diene, such as butadiene or isoprene, in an amount of at least 80 mole% on the total monomer content of the elastomeric polymer block. Butadiene and isoprene are the preferred dienes, but other suitable conjugated dienes include dienes with from 4 to 8 carbon atoms per monomer, for example, 2-ethyl-1,3-butadiene, 2,3-dimethyl-1,3-butadiene, 1,3-butadiene, 1,3-pentadiene, 2,4-hexadiene, 3-ethyl-1,3-pentadiene, and mixtures thereof. Comonomers, if present, may be selected from vinylaromatic monomers and other compounds copolymerizable with the diene.

The vinyl content of the elastomeric polymer block (i.e. that part of the conjugated diene that is polymerized in a "1,2-fashion") is preferably at least 55% (mol/mol on total conjugated diene), more preferably in the range of 65-80%. These styrenic block copolymers have greater ease of processing, require even less plasticizer, and add increased melt strength and drawability to the thermoplastic elastomer composition.

Still more preferred, are styrenic block copolymers that have at least one elastomeric polymer block made of polymerized conjugated diene that is hydrogenated. In

other words, the hydrogenated version of the block copolymers mentioned above. Suitably, such block copolymers are selectively hydrogenated (i.e., only the elastomeric polymer blocks), to a degree of 80% or more based on the (original) residual unsaturation.

Excellent synthetic bottle stoppers have been made from styrenic block copolymers having an overall content of vinylaromatic monomer in the range of 10 to 50% by weight, preferably 20 to 45% by weight. Most preferred are such styrenic block copolymers having a total apparent molecular weight in the range from 30,000 to 400,000 g/mol, more preferably from 50,000 to 300,000 as measured with gel permeation chromatography (GPC) using polystyrene calibration standards (according to ASTM D 3536).

Block copolymers come in the form of linear diblocks, triblocks and multiblocks (produced with sequential polymerization techniques or difunctional coupling agents), or branched block copolymers (using multifunctional coupling agents and/or re-initiation techniques). The preferred block copolymers in accordance with the present invention are linear triblock copolymers, or blends of triblock copolymers, containing up to 30% weight/weight of diblock copolymers.

Suitable block copolymers include, amongst others, those sold by Shell under the trademark "KRATON", and those sold under the trademarks "DYNAFLEX" (CC&P), "VECTOR" (DECXO), "EUROPRENE" (ENICHEM); "QUINTAC" (NIPPON ZEON); "FINAPRENE" (FINA); "STEREON" (FIRESTONE); "TUFRENE" (ASAHI) and "SEPTON" (KURARAY). Particularly suitable are "KRATON" elastomeric block copolymers sold as grade D1102, KX225, G1650, G1652, G1657, G1701, G1726, G1730, G1750 and G1780.

Component b)

A branched polyolefin is a polymer having alkyl groups containing 2 or more carbon atoms attached to the backbone. Such polyolefins are known as high melt strength polymers and hence impart high melt strength and drawability to blends thereof with (styrenic) block copolymers. Such branched polyolefins include e.g., high melt strength propylene polymers, containing long-chain branches inside the polypropylene, disclosed by Dr. Ulf Panzer at the SPO '98; and poly-1-butylene as disclosed in e.g., US Patent No. 4,960,820 which is herein incorporated by reference. Suitable polyolefins have a melt flow index ('MFI') of from 0.05 to 400, preferably from 0.1 to 200, even more preferably from 0.2 to 20 and most preferably from 0.4 to 5 dg/min at 2.16 kg/190 °C. They may be produced by the polymerisation of an alpha- or internal alkene having 3 or more carbon atoms using the Daploy process disclosed by Dr. Pzanzer, or by (Ziegler-Natta low pressure) polymerization of an alpha- or internal alkene having 4 to 10 carbon atoms, preferably a linear alkene such as 1-butene, 1-pentene, 2-pentene, 1-hexene, 1-heptene, 1-octene, or the copolymerization of these alkenes with e.g., up to 10 mole% ethene and/or propene (e.g., as described in DE-A-1,570,353). Preferably the branched polyolefin contains from 80%, more preferably from 95% and most preferably from 97% by weight of isotactic portions. Branched polyolefins that have been found to be very suitable are polymers of 1-butene, having a 1-butene content of at least 50 mole%, preferably at least 70 mole%. The most preferred branched polyolefin is poly-1-butene.

The weight average molecular weight of the polyolefin may range from 60,000 to 1,000,000 g/mol, determined by GPC, using poly-1-butene standards. Suitable polyolefins

have a density of from 0.875 to 0.925, preferably from 0.900 to 0.920 and most preferably from 0.910 to 0.915.

Poly-1-butene PB-0110, marketed by Shell is a particularly suitable polymer. This polymer is a homopolymer with a melt index of 0.4 g/10min. at 190 °C and 2.16 kg and a weight average molecular weight of 800,000.

Component b) is preferably used in an amount of 10 to 100 parts per 100 parts of component a) ('phr'), more preferably in an amount of 30 to 80 phr.

Component c)

Plasticisers are well known to those skilled in the art. Typically, the hardness of polymer compound is decreased by adding a plasticiser. The plasticiser is typically substantially compatible with at least the elastomeric polymer blocks of the thermoplastic block copolymer used as component a).

Examples of plasticisers commonly used in respect of the preferred elastomeric block copolymers include hydrocarbon oil, preferably naphthenic or paraffinic oil, more preferably paraffinic oil. Examples of alternative plasticisers which may be used in the compound of the invention are, oligomers of randomly or sequentially polymerised styrene and conjugated diene, oligomers of conjugated diene, such as butadiene or isoprene, liquid polybutene-1, and ethylene-propylene-diene rubber, all having a weight average molecular weight in the range from 300 to 35,000, preferably from 300 to 25,000, more preferably from 500 to 10,000.

Whereas the presence of such plasticisers in the prior art formulations is essential, as in mentioned herein before with respect to the Supreme Corq bottle stoppers, the presence thereof in the present formulation is only optional, and in the preferred embodiment even absent. If present, then such plasticisers may be used in

an amount of up to 50 phr, preferably in an amount of up to 30 phr, more preferably in an amount of up to 20 phr.

Blowing agent

As noted above the foamed thermoplastic elastomer composition of the present invention also contains a blowing agent. Normally a blowing agent decomposes above a certain temperature thereby releasing gas, such as nitrogen, which causes a volume increase of the reaction mass. The temperature at which the blowing agent starts decomposing is further referred to as the activation temperature. In principle, any known blowing agent such as the ones mentioned above, and more particular as described in US patent No. 5,585,411 may be used. Generally known blowing agents are for instance sodium bicarbonate, azodicarbonamide-based compound and diphenyloxide-4,4'-disulphohydrazide. The latter is commercially available under the tradename "GENITRON" OB, while an azodicarbonamide-based masterbatch is commercially available under the tradenames "GENITRON" PB10 or "CELOGEN" 754A.

Alternative blowing agents are heat expandable thermoplastic particles encapsulating heat expandable gas or liquified gas. Such heat expandable thermoplastic particles are known in the art and available commercially under the tradename "EXPANCEL". Further details regarding such heat-expandable thermoplastic particles can e.g. be obtained from European patent application No. 717,091, which is incorporated herein by reference.

Preferably, the blowing agent is azodicarbonamide or sodium bicarbonate or mixtures thereof. Especially good results may be obtained with sodium bicarbonate.

The blowing agent is preferably present in an amount from 1 to 10 %wt., basis the total composition, more preferably 1 to 5% by weight.

Other components

Optionally, the foamed thermoplastic elastomer composition comprises further components. Such other components include the "olefinic rubbers" mentioned in US patent No. 5,585,411; the compatible and incompatible materials mentioned in WO 94/28066, etc.

For instance, the composition may further comprise from 5 to 50 phr of a polyolefin other than the branched polyolefin, e.g., selected from polyethylene, polypropylene and copolymers thereof. Preferably, the polyolefin is polypropylene or polyethylene, in particular LLDPE. More preferably, the polyolefin is polypropylene.

The foamed thermoplastic elastomer composition may also comprise polymers that are compatible with the glassy polymer blocks of the thermoplastic block copolymers, such as polyphenylene ether and/or polystyrene. For instance, the composition may comprise from 5 to 50 phr of such polymers.

It will be appreciated that the compounds of the present invention may further contain additional compounds like stabilisers, fillers, slipping agents (compounds that are known to provide grip to the glass, such as stearates, eureamide and/or kenamide), waxes and colouring agents (pigments) and even bits of natural cork to give the stopper a cork-like appearance.

The compositions of the invention can be prepared according to procedures well known to those skilled in the art. For instance they may be made by extrusion and melt blending. Examples of apparatus which may be used to prepare the compositions of the present invention include, but are not limited to, single or multiple screw extruders, mixing rollers, internal mixers, Banbury mills, and kneaders. For example, the compositions of the present invention may be prepared by feeding ingredients

either partly or fully as a pre-blend or separately in a discontinuous or continuous mixer. The mixer is preferably a continuous mixer. If in first instance compositions are produced that do not contain a blowing agent then we prefer a twin-screw extruder is used, in particular a co-rotating twin-screw extruder.

The composition ingredients are preferably pre-blended as follows. If a plasticiser is used, then first the block copolymer is blended with part or all of the plasticiser. The latter is preferred. The plasticiser and block copolymer may be blended by contacting the plasticiser and oil and rolling, tumbling or mixing in suitable apparatus. Alternatively, the block copolymer and plasticiser may be melt mixed using apparatus such as single or multiple screw extruders, mixing rollers, internal mixers, Banbury mills, and kneaders. If pre-blending block copolymer and plasticiser is conducted in an extruder, then the plasticiser is typically metered into the extruder such that the metering rate is matched to the proportion of oil and polymer desired in the final composition.

The pre-blending step is typically carried out in a so-called turbo-mixer, such as a "Papenmeier" mixer.

The block copolymer or blend of block copolymer and plasticiser is then blended with the branched polyolefin (e.g., poly-1-butene), and any other ingredients such as filler, polyolefin, polyphenylene ether, syndiotactic polystyrene, stabilisers, waxes and/or pigments. Subsequently, blowing agent may be added, either in the same or a separate blending step. Alternatively, and most preferably, no blowing agent is added at this stage and first a composition without blowing agent is produced.

If a composition without blowing agent is produced, then the composition may subsequently be pre-blended or tumble-mixed with a blowing agent to prepare a

masterbatch as will be discussed in more detail herein after.

5 If a composition with blowing agent is produced, care should be taken that during the compounding process the temperature is kept below the blowing agent decomposition temperature unless (full or partial) foaming is desired during this first step.

10 The preparation of a foamed thermoplastic elastomer composition as described above comprises a second aspect of the present invention. In order to produce the "cork", the composition is injected into a mould, e.g. as described in US patents Nos. 3,984,022 and/or 4,499,141. Alternatively, the present composition allows corks to be made via extrusion, which is much preferred over
15 injection moulding since producing uniform corks in a continuous fashion at a higher rate. A third aspect of the present invention concerns foamed articles (including, but not limited to corks) obtainable by this preparation.

20 The invention is illustrated by the following examples.

Examples

The following ingredients were used in the Examples:

PF814	a high melt strength polypropylene (MFI = 3, 230 °C/2.16 kg) commercially available from Montell polyolefins.
PB0110	a high melt strength poly-1-butene (MFI = 0.4, 190 °C/2.16 kg; MP is about 125 °C) commercially available from Montell polyolefins.
"PRIMOL" 352	Paraffinic oil.
"KRATON" G1652 ('KG1652')	a linear styrene-ethylene/butylene-styrene block copolymer having a polystyrene content of 29% by weight, available from Shell Chemicals companies.
"KRATON" G1701 ('KG1701')	a linear styrene-ethylene/propylene block copolymer having a polystyrene content of 28% by weight, available from Shell Chemicals companies.
"IRGANOX" 1010	tetrakis-ethylene-(3,5-di-tertiary-butyl-4-hydroxy-hydrocinnamate)methane.
"IRGANOX" PS800	dilauryl thiopropionate.
"GENITRON" PB10	a masterbatch of 10% weight azodicarbonamide in a LDPE carrier, available from Bayer.
"CELOGEN" 754-A	activated azodicarbonamide in powder form, available from Uniroyal Chemicals.

TPE Compositions

Compositions not containing blowing agent were prepared as follows. 100 parts by weight of a KG1652 were blended with a desired amount (0 or 30 parts by weight,

phr) of "PRIMOL" 352 in a Papenmeier mixer for 10 minutes at room temperature.

To the pre-blend thus obtained were added the desired amount (0 or 25 phr) of KG1701, a desired amount (27 or 54 phr) of poly-1-butene and a desired amount (0 to 54 phr) of polypropylene and stabilisers. Blending was continued for 5 minutes.

The pre-blend thus obtained was fed into a co-rotating twin-screw extruder (Werner-Pfeifferer) to produce various compositions. The temperature in the twin-screw extruder ranged from 140 to 200 °C. The twin-screw extruder is equipped with a strand die. The strands obtained are cooled down in a water bath and cut into pellets with a pelletiser. Table 1 depicts the breakdown of compositions A-D, all in parts by weight.

Table 1

Compound	A	B	C	D
KG1652	100	100	100	100
KG1701		25	25	25
"PRIMOL" 352				30
PB0110	54	54	54	27
PF814		54	27	27
"IRGANOX" 1010	0.2	0.2	0.2	0.2
"IRGANOX" PS800	0.2	0.2	0.2	0.2

Pellets of compositions A and B obtained above were dry-blended with 3% by weight of azodicarbonamide as blowing agent to prepare masterbatches A and B. The blowing agent used in example 1 was "GENITRON" PB10.

The masterbatches A and B thus obtained were fed into a single screw lab extruder (Extrudex), using a temperature profile of 190 °C at the feed entrance, 200 °C at the end of the extruder and 210 °C at the die, to prepare foamed compositions A and B. The die was a

strand die of 6 mm. The density of the foamed strands obtained and the compounds prior foaming were measured. Results are shown in Table 2.

Table 2

Compound	Density
A prior foaming	0.90
A + 3% blowing agent	0.66
B prior foaming	0.91
B + 3% blowing agent	0.54

5 Both compositions A and B show a good density decrease with 3% of blowing agent. The best density decrease is obtained with composition B containing a mixture of triblock and diblock copolymers.

Example 2

10 Pellets of compositions A and B obtained in example 1 were dry-blend with 2.5 or 3% by weight of "GENITRON" PB10 as a blowing agent to prepare masterbatches.

15 The masterbatches thus obtained were fed into an injection moulding machine (Battenfeld), using a temperature profile of 190 °C at the feed entrance 200 °C at the end of the extruder and 210 °C at the die, to prepare foamed specimen A and B. The foamed specimen obtained by the injection were circular plates with a diameter of 45 mm and a thickness of 6 mm. The density of the foamed specimen were measured and the results are
20 shown in Table 3.

Table 3

Composition	Density
A + 2.5% blowing agent	0.53
B + 2.5% blowing agent	0.52
B + 3% blowing agent	0.52

Both compounds show good density decrease with 2.5% by weight of blowing agent and an increase of blowing agent did not result in a decrease of the density.

Example 3

5 Pellets of compositions A, C and D were dry-blended with 5% by weight of azodicarbonamide as blowing agent to prepare masterbatches A, C and D. The masterbatch A and C has been prepared with the blowing agent "GENITRON" PB10. The masterbatch D has been prepared with the blowing agent "CELOGEN" 754-A.

10 The masterbatches A, C and D thus obtained were fed into an injection moulding machine (Negri Bossi & C), using a temperature profile of 170 °C at the feeding entrance, 190 °C at the end of the extruder and 190 °C at the die to prepare foamed specimens A and C. The temperature profile was 160 °C at the feeding entrance and 180 °C at the end of the extruder and at the die to prepare specimens D. The foamed specimens obtained were stoppers of 38 mm by length and a diameter of 22 mm. The density of the stoppers were measured and the results are shown in Table 4.

Table 4

Composition	Density
A + 5% blowing agent	0.63
C + 5% blowing agent	0.56
D + 5% blowing agent	0.54

The best density decreases were obtained with compositions C and D, containing linear styrene-ethylene/propylene block copolymer.

25 The foaming conditions have not been optimised in examples 2 and 3. For instance, optimisation of foaming conditions such as optimum temperature profile and die

pressure is expected to lead to further density reduction to e.g. 0.5.

It is known that poly-1-butene crystallises only slowly. If desired, nucleating agents may be used to increase the crystallisation rate. Nucleating agents are well known to those skilled in the art and available commercially. The most popular nucleating agent is Talc, but the use of stearamide is also well known.

Example 4

Foamed stoppers C and D thus obtained in example 3 have been inserted in glass bottles filled with water, using a manual cork insertion machine. An ordinary corkscrew was then fixed into the stoppers. The bottles have been then fixed in a tensile machine (Zwick) while the corkscrew was fixed at the moving crosshead. The stoppers were pull-out of the bottle at a constant speed of 100 mm/min. The force needed to extract the stoppers was measured and the wall-stress was calculated with the stopper length and the bottle circumference. The stoppers C and D have been measured in comparison with natural cork of 3 and 5 years old and in comparison with competitor synthetic stoppers X and Y, having both a density of 0.60. The results are shown in Table 5.

Table 5

Stoppers	Force N	Wall Stress, kPa
Natural cork 3 years	247	156
Natural cork 5 years	395	153
Competitor X	230	110
Competitor Y	180	70
Stopper C	410	184
Stopper D	230	112

The curves obtained during the tensile test are shown in figure 1. The results and the graph show that stopper C is closer to the natural cork of 3 or 5 years.

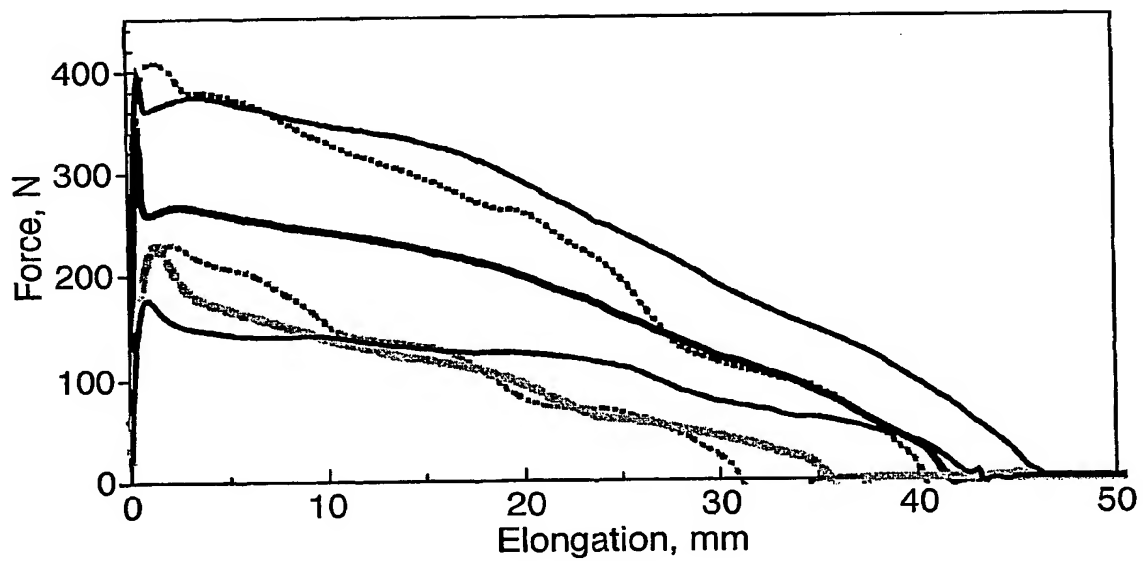
C L A I M S

1. A synthetic bottle stopper made from a foamed thermoplastic elastomer composition comprising
 - a) one or more thermoplastic block copolymers
 - c) a blowing agent, and optionally
 - 5 d) one or more plasticisers,characterised in that the composition further comprises
 - b) one or more branched polyolefins having a melt flow index of from 0.05 to 400 (at 2.16 kg/190 °C, determined in accordance with ASTM D 1238).
- 10 2. A synthetic bottle stopper as claimed in claim 1, comprising one or more styrenic block copolymers as component a), wherein the or each styrenic block copolymer contains one or more glassy polymer blocks made of polymerized vinylaromatic monomer in an amount of at least 80 mole% on the total monomer content of the block and having one or more elastomeric polymer blocks made of polymerized conjugated diene in an amount of at least 80 mole% on the total monomer content of the block.
- 15 3. A synthetic bottle stopper as claimed in claim 2, wherein the vinylaromatic monomer is styrene and wherein the diene is butadiene and/or isoprene.
- 20 4. A synthetic bottle stopper as claimed in claims 2 to 3, wherein the or each styrenic block copolymer has an overall content of vinylaromatic monomer in the range of 10 to 50% by weight, and a total apparent molecular weight in the range of from 30,000 to 400,000 g/mol.
- 25 5. A synthetic bottle stopper as claimed in claims 1 to 4, wherein component a) comprises a triblock polymer or a mixture of a diblock and triblock copolymer.

6. A synthetic bottle stopper as claimed in claims 1 to 5, wherein component b) comprises a polymer of 1-butene and/or a high melt strength polymer of propene.
- 5 7. A synthetic bottle stopper as claimed in claim 6, comprising component b) in an amount of 10 to 100 parts by weight per 100 parts by weight of component a).
8. A synthetic bottle stopper as claimed in claims 1 to 7, comprising a blowing agent in an amount from 1 to 10 %wt, basis the total composition.
- 10 9. A process for preparing a foamed thermoplastic elastomer composition comprising
- a) one or more thermoplastic block copolymers
- b) one or more branched polyolefins having a melt flow index of from 0.05 to 400 (at 2.16 kg/190 °C, determined
- 15 in accordance with ASTM D 1238)
- c) a blowing agent, and optionally
- d) one or more plasticisers,
- wherein components a) to d) are fed either partly or fully as a pre-blend or separately in a discontinuous or
- 20 continuous mixer.
10. A foamed article obtainable by the process of claim 9.

Fig.1.

— Natural cork 3 years — Natural cork 5 years - - - Stopper C
- - - Stopper D - - - Competitor X — Competitor Y



INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 00/06354

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 B65D39/00 C08J9/00 C08L53/00 C08L23/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B65D C08J C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

EPO-Internal, CHEM ABS Data, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	WO 00 26103 A (PLIMMER PETER N ; SUPREME CORQ INC (US); ZECH JEROME M JR (US)) 11 May 2000 (2000-05-11) claims; examples	1-10
P,X	WO 00 12592 A (SHELL INT RESEARCH) 9 March 2000 (2000-03-09) claims; examples	1-10
X	US 5 496 862 A (BURNS DENNIS L) 5 March 1996 (1996-03-05) cited in the application column 3, line 60 - line 67; figures column 4, line 53 - line 63 column 5, line 53 - column 6, line 2; claims	1-6, 8-10



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents:

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X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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& document member of the same patent family

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 00/06354

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 00/06354

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